

Structural study of the $\text{Lu}_2\text{Si}_2\text{O}_7$ – $\text{Sc}_2\text{Si}_2\text{O}_7$ system

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Abstract

Different compositions in the $\text{Lu}_2\text{Si}_2\text{O}_7$ – $\text{Sc}_2\text{Si}_2\text{O}_7$ system have been synthesized following the ceramic method. All XRD patterns are compatible with the thortveitite structure (β - $\text{RE}_2\text{Si}_2\text{O}_7$ polymorph). Unit cell parameters change linearly with composition, which indicates a complete solid solubility of $\text{Sc}_2\text{Si}_2\text{O}_7$ in $\text{Lu}_2\text{Si}_2\text{O}_7$. ^{29}Si MAS NMR spectra show a decrease of the ^{29}Si chemical shift with increasing Sc content. A correlation reported in the literature to predict ^{29}Si chemical shifts in silicates is applied here to obtain the theoretical variation in ^{29}Si chemical shift values in the system $\text{Lu}_2\text{Si}_2\text{O}_7$ – $\text{Sc}_2\text{Si}_2\text{O}_7$ and the results compare favourably with the values obtained experimentally. The FWHM values of the ^{29}Si MAS NMR curves indicate a random distribution of Lu and Sc in the structure of the intermediate members. Finally, the IR study of the system confirms the solubility of $\text{Sc}_2\text{Si}_2\text{O}_7$ in $\text{Lu}_2\text{Si}_2\text{O}_7$, showing the splitting of several modes in the intermediate members and a linear shift of the frequency on going from one end-member to the other.

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1. Introduction

Rare earth (RE) pyrosilicates ($\text{RE}_2\text{Si}_2\text{O}_7$) are well known for their polymorphism. They exhibit up to eight structure types (at normal pressure) depending on the temperature and the ionic radius of the RE cation [1,2]. All of them contain $(\text{Si}_2\text{O}_7)^{6-}$ structural units (two silicon tetrahedra sharing one corner), except the α -polymorph which has the average pyrosilicate composition but contains $(\text{SiO}_4)^{4-}$ and $(\text{Si}_3\text{O}_{10})^{8-}$ anions in 1:1 ratio.

Many structural studies have been conducted on RE pyrosilicates containing one type of RE cation. The investigation of the solid solubility between $\text{RE}_2\text{Si}_2\text{O}_7$ structures containing different RE cations has been, however, very scarce [2,3]. The study of this subject is interesting, not only under an academic point of view, but also in the materials science field. Mixtures of refractory RE oxides are used as sintering aids for the fabrication of silicon nitride structural ceramics. Upon annealing, $(\text{RE})_2\text{Si}_2\text{O}_7$ crystallizes at the grain boundaries of Si_3N_4 , and

improves the high temperature mechanical properties of the material [4–9]. Knowledge of the crystalline structures adopted by the $(\text{RE})_2\text{Si}_2\text{O}_7$ intergranular phase at different temperatures and RE contents is, therefore, of great value in understanding the behaviour of these materials. Several researchers have shown that the high temperature strength and oxidation resistance of Si_3N_4 are correlated with the radius of the RE cation in the oxide additives, such that the smaller the RE the better the properties of the silicon nitride [9,10]. Choi and Lee [10] showed that Y_2O_3 , Lu_2O_3 and Sc_2O_3 , among all lanthanide oxides, impart the highest flexural strength values to Si_3N_4 .

In this paper, we have selected the last two oxides to examine the structures across the $\text{Lu}_2\text{Si}_2\text{O}_7$ – $\text{Sc}_2\text{Si}_2\text{O}_7$ system; members of this system are expected to form in the intergranular region of Si_3N_4 when mixtures of both oxides are used as sintering aids of the Si_3N_4 structural ceramic. Both $\text{Lu}_2\text{Si}_2\text{O}_7$ and $\text{Sc}_2\text{Si}_2\text{O}_7$ (the latter is the thortveitite mineral) exhibit a unique crystalline form at any temperature, called β -polymorph or thortveitite-type structure, which will simplify the study. We have studied the long- and short-range order variations of the structures appeared with increasing Sc content from pure $\text{Lu}_2\text{Si}_2\text{O}_7$ to

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pure $\text{Sc}_2\text{Si}_2\text{O}_7$ by means of X-ray diffraction (XRD), ^{29}Si nuclear magnetic resonance (NMR) spectroscopy and infrared (IR) spectroscopy.

2. Experimental

Preparation of the samples: The following compositions in the system $\text{Lu}_2\text{Si}_2\text{O}_7$ – $\text{Sc}_2\text{Si}_2\text{O}_7$ were synthesized by solid-state reaction using a SiC resistance furnace: 0, 25, 50, 70, 75, 80, 85, 90, 95 and 100 mol% $\text{Sc}_2\text{Si}_2\text{O}_7$. Starting materials were Lu_2O_3 (99.5%), Sc_2O_3 (99.9%) and SiO_2 (99.8%). The mixtures were ground in an agate mortar with ethyl alcohol and sintered in Pt crucibles at 1 atm and 1550 °C. Grinding and heat treatments were repeated when necessary to obtain clear XRD patterns.

Characterization: XRD diagrams were registered under the following conditions: scan speed = 1°/2 min, chart speed = 2 cm/min, scan range = 25° < 2 θ < 70° with $\text{CuK}\alpha$. NaCl was used as an internal standard. The XRD patterns were analysed using the GSAS software [11], in order to obtain unit cell parameters. Single-pulse ^{29}Si NMR spectra under magic angle spinning (MAS) were recorded on a Bruker DRX400 spectrometer equipped with a multi-nuclear probe using a magnetic field of 9.36 T. Powdered samples were packed in 4 mm zirconia rotors and spun at 12 kHz. The spectra were acquired at a frequency of 79.49 MHz using a $\pi/6$ pulse width of 2.66 μs and a pulse space of 600 s. Chemical shifts are reported in ppm from Tetramethylsilane. IR Fourier Transform (FT) spectra were obtained using a Nicolet 510 FTIR instrument equipped with a DTGS detector. Spectra were recorded in the 1500–400 cm^{-1} range with a resolution of 2 cm^{-1} . The measurements were made using dried KBr pellets, which were prepared by mixing and pressing 1.5 mg of sample with 100 mg KBr.

3. Results and discussion

3.1. XRD study

The XRD diagrams of all samples in the system $\text{Lu}_2\text{Si}_2\text{O}_7$ – $\text{Sc}_2\text{Si}_2\text{O}_7$ showed exclusively diffractions from thortveitite [12], with intensity and position of the peaks varying with composition as a result of the different X-ray scattering factors and sizes of Lu^{3+} and Sc^{3+} (ionic radii in octahedral coordination: $\text{Lu}^{3+} = 0.861 \text{ \AA}$ and $\text{Sc}^{3+} = 0.745 \text{ \AA}$) [13]. In order to obtain the variation of structural parameters with composition, the XRD patterns of all compositions were analysed using the Le Bail method with the GSAS software, as described in the experimental section. The starting parameters for the refinement of the structures with % mol $\text{Sc}_2\text{Si}_2\text{O}_7 \geq 50\%$ have been taken from those reported for pure $\beta\text{-Sc}_2\text{Si}_2\text{O}_7$ [14] while the refinement of compositions with % mol $\text{Sc}_2\text{Si}_2\text{O}_7 \leq 50\%$ was carried out from the parameters reported for pure $\beta\text{-Lu}_2\text{Si}_2\text{O}_7$ [15]. In both cases, space group $C2/m$ has been used. Fig. 1 shows the unit cell parameters as a function of

Sc content. The same size of the y -axis has been used in the plots of a , b and c unit cell parameters in order to appreciate relative changes. Both a and b unit cell parameters decrease linearly with increasing Sc content, while c does not change appreciably with composition. The β -angle increases with increasing Sc content, the total variation in the angle from one end-member to the other being less than 1°. Finally, the unit cell volume decreases linearly with increasing Sc content, with a total variation in volume of 23.9 $\text{\AA}^3$. This behaviour is qualitatively very similar to that of other thorveitite system, $\beta\text{-Lu}_2\text{Si}_2\text{O}_7$ – $\beta\text{-Y}_2\text{Si}_2\text{O}_7$ [3a], although the unit cell volume change in that case was much smaller ($\sim 10 \text{ \AA}^3$) as a consequence of the lower difference in size of the RE^{3+} ions (Y^{3+} ionic radii in octahedral coordination: 0.900 $\text{\AA}$).

The unit cell parameters behaviour in the system $\text{Lu}_2\text{Si}_2\text{O}_7$ – $\text{Sc}_2\text{Si}_2\text{O}_7$ indicates the existence of a complete series of solid solutions from $\text{Lu}_2\text{Si}_2\text{O}_7$ to $\text{Sc}_2\text{Si}_2\text{O}_7$ (at least at 1550 °C which is the sintering temperature of this study).

3.2. ^{29}Si MAS–NMR study

The local environment of the Si nuclei in the members of the $\text{Lu}_2\text{Si}_2\text{O}_7$ – $\text{Sc}_2\text{Si}_2\text{O}_7$ system has been studied by means of ^{29}Si MAS–NMR spectroscopy; the spectra of the different compositions are shown in Fig. 2. All the spectra show a unique band in the ppm range characteristic of the Q¹ environments of the $[\text{Si}_2\text{O}_7]^{6-}$ units in the pyrosilicate structure.

The FWHM values have been plotted versus composition in Fig. 3a. The distribution of Lu and Sc in the $\beta\text{-RE}_2\text{Si}_2\text{O}_7$ crystal structure plays an important role in the FWHM values of the NMR peaks. Each silicon nucleus in the $\beta\text{-RE}_2\text{Si}_2\text{O}_7$ structure is surrounded by six ORE ligands, i.e. $\text{Si}(\text{6OLu})$ and $\text{Si}(\text{6OSc})$ are the Si environments in pure $\text{Lu}_2\text{Si}_2\text{O}_7$ and $\text{Sc}_2\text{Si}_2\text{O}_7$, respectively. A homogeneous ordered distribution of Lu and Sc atoms in the crystal structure would cause a unique type of Si environment in the $\text{LuScSi}_2\text{O}_7$ composition (50% $\text{Sc}_2\text{Si}_2\text{O}_7$ in $\text{Lu}_2\text{Si}_2\text{O}_7$)—namely $[(\text{Sc,LuO})]_3\text{-Si-O-Si-}[(\text{Sc,LuO})]_3$. On the contrary, a random distribution of Lu and Sc in the crystal structure would give rise to 7 different types of Si environments in any composition, the proportions of each depending on the Lu/Sc ratio. This variety of environments would give rise to a maximum FWHM value in the spectrum of $\text{LuScSi}_2\text{O}_7$ while the FWHM value would decrease when crossing to both end members. The latter seems, therefore, to be the case of our system. The difference in FWHM shown by the two end-members is very likely due to the higher quadrupolar moment of ^{175}Lu compared to ^{45}Sc on the Si environment (^{175}Lu : $I = 7/2$, $Q = 349 \text{ fm}^2$; ^{45}Sc : $I = 7/2$; $Q = -22 \text{ fm}^2$), which gives a more efficient relaxation to the ^{29}Si nucleus. Heating at higher temperatures does not change the FWHM values in the end-members.

It can be easily observed from Fig. 2 that the maxima of the spectra shift to lower frequency with increasing Sc

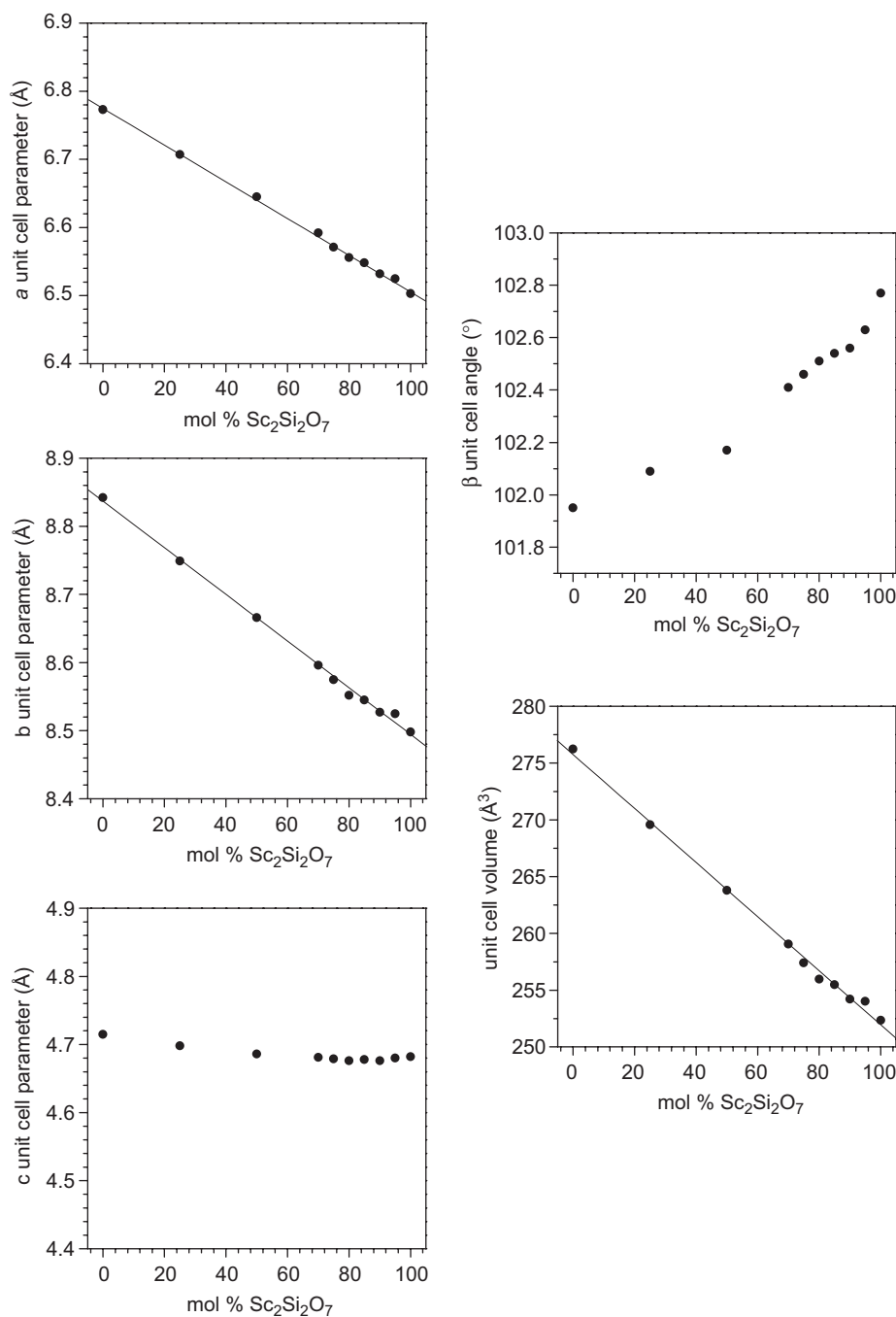


Fig. 1. Unit cell parameters (a , b , c , β and volume) plotted as a function of Sc content in the $\text{Lu}_2\text{Si}_2\text{O}_7$ – $\text{Sc}_2\text{Si}_2\text{O}_7$ system. The error bars are approximately the size of the symbols.

content; such maxima have been plotted versus Sc content in Fig. 3b, where a quasi-linear dependence is observed. The ^{29}Si chemical shifts of the end members are in agreement with the values reported in the literature for $\text{Lu}_2\text{Si}_2\text{O}_7$ [16] and $\text{Sc}_2\text{Si}_2\text{O}_7$ [17]. Janes and Oldfield [18] proposed a linear relation between group electronegativity (EN) sums of ligands bonded to tetravalent silicon and ^{29}Si NMR chemical shift values. This correlation applies well to the solid solution β - $\text{Lu}_2\text{Si}_2\text{O}_7$ – β - $\text{Y}_2\text{Si}_2\text{O}_7$ recently reported

by us [3a]. The following section of this work is devoted to check that the chemical shift values obtained for the system under study also follows Janes and Oldfield's correlation. This will allow establishing a model of distribution of Lu and Sc in the β - $\text{RE}_2\text{Si}_2\text{O}_7$ crystal structure, which supports or denies the predictions made from the FWHM behaviour in Fig. 3a.

For type P silicon sites, as is the case for our pyrosilicate structure, Janes and Oldfield [18] give the following

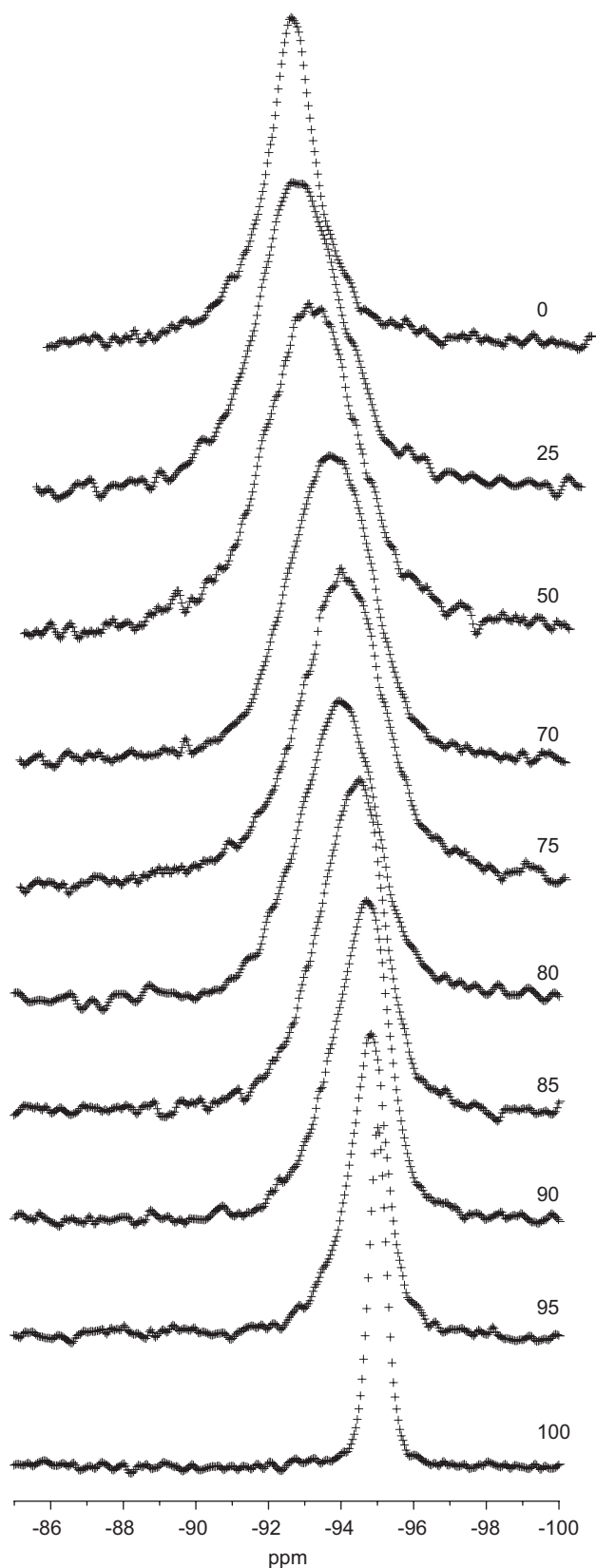


Fig. 2. Experimental ^{29}Si MAS-NMR spectra of samples in the $\text{Lu}_2\text{Si}_2\text{O}_7$ - $\text{Sc}_2\text{Si}_2\text{O}_7$ system. Numbers indicate the mol% of $\text{Sc}_2\text{Si}_2\text{O}_7$.

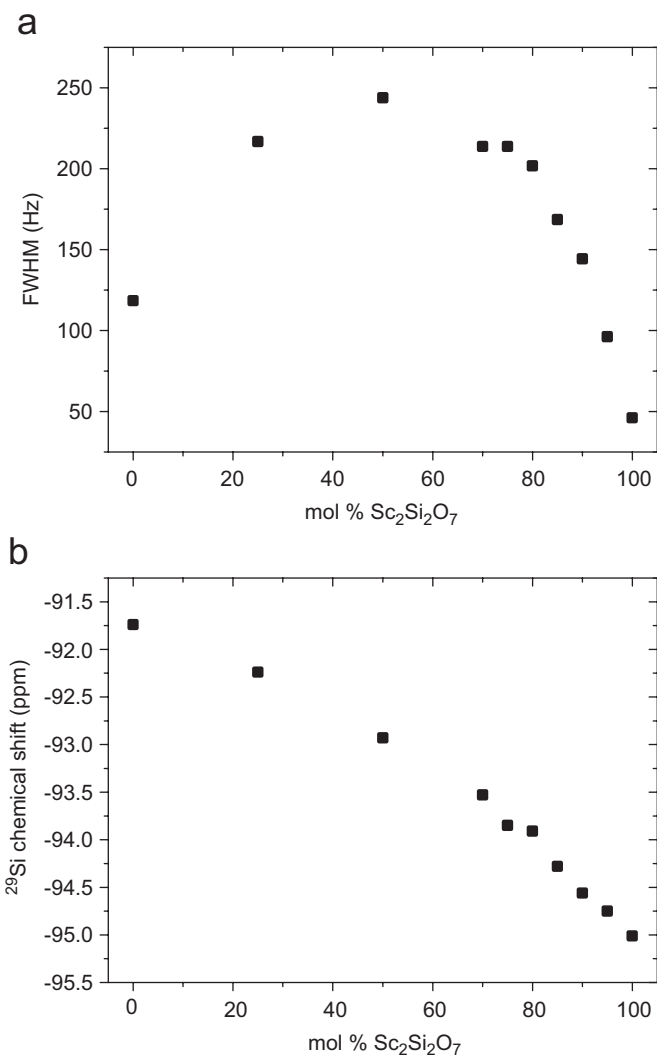


Fig. 3. (a) FWHM values of the ^{29}Si MAS-NMR spectra as a function of Sc content in the $\text{Lu}_2\text{Si}_2\text{O}_7$ - $\text{Sc}_2\text{Si}_2\text{O}_7$ system. (b) Experimental ^{29}Si chemical shift values plotted as a function of Sc content in the $\text{Lu}_2\text{Si}_2\text{O}_7$ - $\text{Sc}_2\text{Si}_2\text{O}_7$ system.

correlation:

$$\delta_{\text{Si}} = -24.336 \sum \text{EN} + 279.27, \quad (1)$$

where $\sum \text{EN}$ is the group EN sum. In order to calculate EN sums, the group ENs of the oxy-metal ligands (OSi, OLu and OSC) forming the crystal are needed. The EN(OSi) value can be calculated from the linear correlation obtained by Janes and Oldfield between EN(OSi) and the bridging bond angle, which is 180° for pyrosilicate structures. The EN(OLu) value was calculated empirically by us from the ^{29}Si chemical shifts of two model compounds β - $\text{Lu}_2\text{Si}_2\text{O}_7$ and $\text{X2-Lu}_2\text{SiO}_5$ obtaining an average value of 3.6684 [3a]. In order to obtain the EN(OSc) value, we have now to limit ourselves to a model compound containing Si and Sc, with a known ^{29}Si chemical shift value, i.e. β - $\text{Sc}_2\text{Si}_2\text{O}_7$, which gives an EN(OSc) value of 3.7132. We have calculated δ_{Si} values from the EN sums corresponding to each member of the

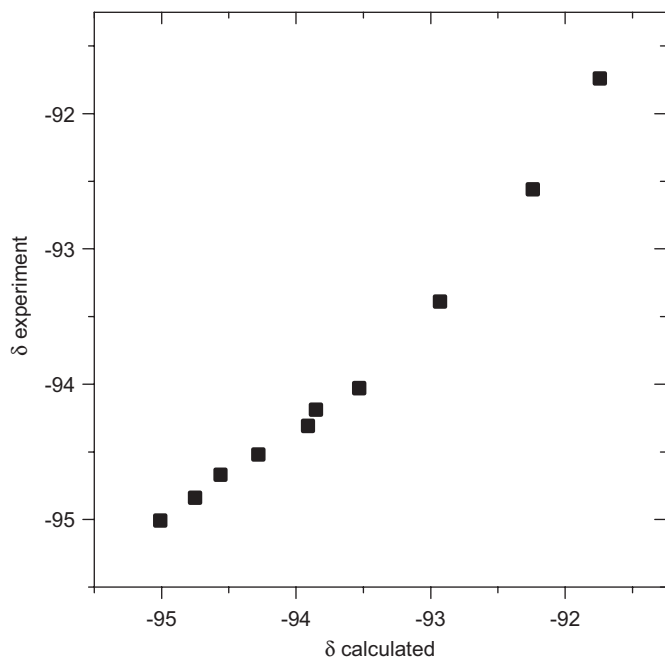


Fig. 4. Experimental ^{29}Si chemical shift values versus the ones predicted from the correlation of Janes and Oldfield [18] using electronegativity group values.

system $\text{Lu}_2\text{Si}_2\text{O}_7\text{--Sc}_2\text{Si}_2\text{O}_7$, as explained for a general case in Janes and Oldfield [18] and for a pyrosilicate system very similar to this one in Becerro and Escudero [3a]. Once calculated the EN sums for all the Si environments expected from a random distribution of Lu and Sc in the silicate crystal structure (as indicated by the FWHM behaviour), we have calculated the ^{29}Si chemical shift values for each composition having into account the % of each Si environment expected from a random distribution of elements in the crystal. The results have been plotted versus the experimental ones in Fig. 4. A high correlation is observed between both sets of values with a correlation coefficient = 0.985, to be compared to 0.979 obtained by Janes and Oldfield in their Fig. 2 [18]. This fact supports at the same time, the model of random distribution of Lu and Sc in the pyrosilicate crystal structure.

3.3. IR study

Fig. 5 shows the IR spectra of samples in the $\text{Lu}_2\text{Si}_2\text{O}_7\text{--Sc}_2\text{Si}_2\text{O}_7$ system in the range $1300\text{--}450\text{ cm}^{-1}$.

The high-frequency region (from 1300 to 700 cm^{-1}) contains the stretching vibrations of Si atoms against oxygen atoms in Si–O–Si bonds as well as the Si–O stretching modes involving apical (non-bridging) oxygens. The IR spectrum of pure $\text{Sc}_2\text{Si}_2\text{O}_7$ has been described by Lazarev [19]; while only three stretching Si–O vibrational modes are allowed in the D_{3d} symmetry, typical of centrosymmetric Si_2O_7 groups, the fall in the site symmetry (to C_{2h}) due to the presence of different Si–O(nbr) distances in the Si tetrahedra, removes the degeneracy $E_u \rightarrow B_u + A_u$, allowing for four Si–O stretching bands (marked with

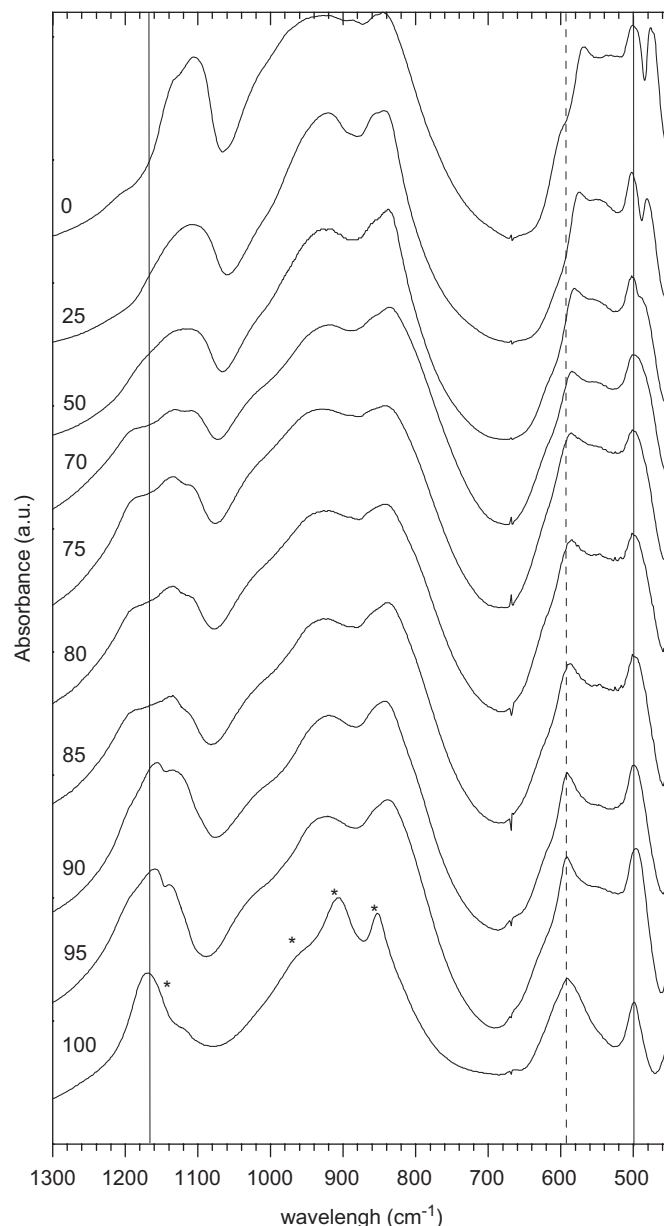


Fig. 5. Infrared absorption spectra of samples in the $\text{Lu}_2\text{Si}_2\text{O}_7\text{--Sc}_2\text{Si}_2\text{O}_7$ system. Numbers indicate the mol% of $\text{Sc}_2\text{Si}_2\text{O}_7$. Vertical lines indicate the shift of several bands with composition, as explained in the text.

asterisks in the spectrum of pure $\text{Sc}_2\text{Si}_2\text{O}_7$). The doublet observed at the highest frequency band has been ascribed to transitions from excited states [19]. Fig. 5 shows a shift of the bands towards lower frequencies (see, for example the band at 1170 cm^{-1}) with increasing Lu content. Likewise, the intermediate members of the solid solution show a splitting of the stretching vibrations, which is observed as a broadening of the bands. Such splitting can be explained in the basis of an increase in the number of different Si–O–RE bonds as a consequence of the presence of both Lu and Sc in these members, which reduces the symmetry of the lattice. This result is in agreement with the conclusions obtained from the analysis of the ^{29}Si NMR spectra.

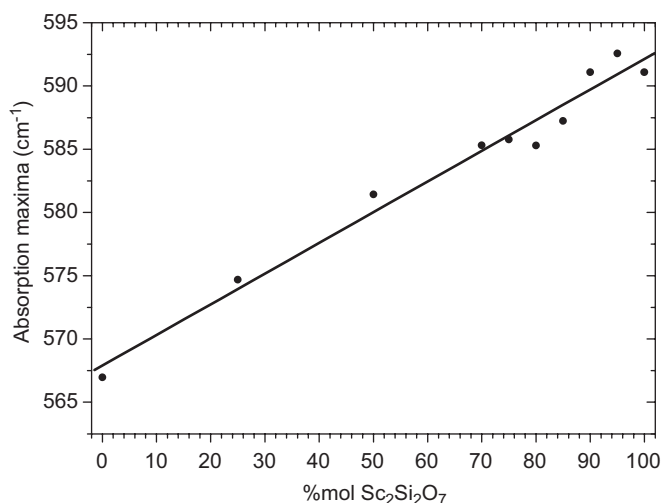


Fig. 6. Shift of the low-frequency vibration, marked with a dashed line in Fig. 5, as a function of Sc content.

Finally, the low-frequency region (from 700 to 450 cm^{-1}) in Fig. 5 is more difficult to characterize because single M–O and Si–O vibrations coexist in that spectral range. Pure $\text{Sc}_2\text{Si}_2\text{O}_7$ shows two bands in this spectral range. While Lazarev [19] assigns the two bands at 591 and 498 cm^{-1} to $\delta'_s\text{SiO}_3$ and $\rho'\text{SiO}_3$, respectively, Diaz et al. [20] assign, in a study of the isostructural $\beta\text{-Y}_2\text{Si}_2\text{O}_7$ compound, the lowest frequency band to a Si–O bending mode and the higher frequency one to Y–O stretching vibrations, which would correspond to RE–O in the case of our solid solution. It can be observed that, while the lower frequency mode does not change position crossing the system from pure $\text{Sc}_2\text{Si}_2\text{O}_7$ to pure $\text{Lu}_2\text{Si}_2\text{O}_7$, the band at 591 cm^{-1} shifts towards lower frequencies with decreasing Scandium content; Fig. 6 shows the absorption maxima versus composition, where a linear dependence is observed.

4. Conclusions

The crystallographic unit cell parameters behave linearly with composition all across the system $\text{Lu}_2\text{Si}_2\text{O}_7\text{--Sc}_2\text{Si}_2\text{O}_7$ at 1550 °C. The analysis of the FWHM values of the ^{29}Si MAS NMR spectra indicates that Sc and Lu atoms are randomly distributed in the crystal structure of the pyrosilicate. The experimental ^{29}Si chemical shift values coincide, within a minimum deviation, with those predicted from EN group values with the correlation proposed by Janes and Oldfield [18]. Finally, the IR study shows several the splitting of several modes with changing the Sc/Lu ratio as well as a shift of the frequency maxima of some of the vibrations examined.

The results allow concluding that a complete solid solution exists from $\text{Lu}_2\text{Si}_2\text{O}_7$ to $\text{Sc}_2\text{Si}_2\text{O}_7$ at 1550 °C from both, long- and short-range order points of view.

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